

DFT Study of O<sub>2</sub> Reduction on Platinum

Reyimjan A. Sidik and Alfred B. Anderson  
Department of Chemistry  
Case Western Reserve University  
Cleveland, OH 44106-7078

Introduction

Due to its importance in energy conversion, particularly in fuel cells, air-batteries, and corrosion, the electrochemical reduction of oxygen (ERO) has been the focus of much research work for well over 3 decades<sup>1</sup>. Experimental data have seemed to suggest a mechanism of the first electron transfer being the rate determining step in acidic media on platinum. Despite the recent progress that has been made in understanding this reaction using in-situ spectroscopic techniques<sup>2</sup>, several questions concerning ERO still lack definite answers. These questions include how O<sub>2</sub> interacts with the electrode surface and what effect reaction intermediate adsorptions have on the rate of reaction, and how they vary with electrode potential. Understanding this reaction at atomistic level, which presumably should help in designing better and cheaper than Pt catalysts, has not yet been achieved. Clearly, additional experimental or theoretical information are needed to establish the mechanism of ERO on platinum.

This lab has recently developed an ab initio theoretical approach that allows us to study the dependence of mechanisms, transition state structures, and activation energies on the electrode potential for electrochemical reactions. This approach has been applied to both redox and catalytic reactions with reasonable success<sup>3,4,5,6</sup>. We have extended this previous work in a DFT study O<sub>2</sub> reduction on Pt<sub>2</sub>.

Theoretical approach

Current electron transfer theory states that electron transfer between an electrode and a solution species near the double layer occurs when the electrochemical energy of an electron in the metal is equal to an acceptor level of the solution species. Thus, in this work, when the electrochemical potential of the electron, i.e., the vacuum scale potential of the electrode, is equal to an acceptor level created by thermal fluctuations in the reactant complex, electron transfer is assumed to take place through radiationless tunneling. The acceptor level in the reactant complex is actually the optical electron affinity (EA) of that complex. Therefore, in order to find a transition state for a given reactant complex at a given electrode potential, U, one distorts the reactant complex to obtain the electron affinity corresponding to the electrode potential and then minimizes the energy of the complex while still maintaining that EA. Effectively, that corresponds to looking for the minimum energy structure on the dividing surface of the reactant and product potential energy surfaces. The advantage of this approach is that one does not need to construct a multi-dimensional potential energy surface for either reactants or products. See Refs. 4,5,6 for details.

Computational Method

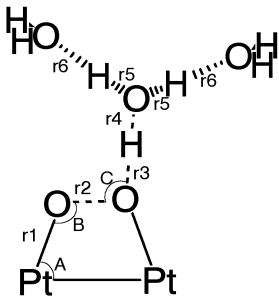
The B3LYP level of theory is used for this work, with 6-31G\*\* basis set for O and H, and LANL2DZ for Pt. A Pt<sub>2</sub> molecule, with a bulk distance of 2.775 Å, is used as the model electrode to coordinate O<sub>2</sub>, OOH, H<sub>2</sub>O, OH, and O intermediates in the oxygen reduction. The

justification for using Pt<sub>2</sub> as the electrode comes from the fact that the calculated adsorption strengths of those intermediates on Pt<sub>2</sub> are comparable to the low-coverage experimental values as shown in the following table.

Bond	1-fold	2-fold	Exper. range
Pt-OH	2.52	2.17	2.5~1.5 <sup>7</sup>
Pt-OH <sub>2</sub>	0.68	0.25	0.65 <sup>8</sup>
Pt-O	3.67	4.53	~3.5, 3.8 <sup>9</sup>

Results and Discussion

Recent in-situ spectroscopic results indicate that the most probable adsorption structure for O<sub>2</sub> on platinum electrode is the parallel di-σ orientation<sup>2</sup>; therefore, we used that mode of adsorption and found an adsorption bond strength of 0.94 eV for O<sub>2</sub> on Pt<sub>2</sub>. A barrier of 0.74 eV was calculated for dissociation of O<sub>2</sub>. However, Pt<sub>2</sub>OOH had small 0.06 eV barrier for breaking the O-O bond to form PtOH + PtO. To account for the presence of counter ion field effects, a -0.5e charge was placed 10 Å away from the H<sup>+</sup> along the H<sup>+</sup>--OH<sub>2</sub> bond. For the activation energy calculations, as shown in the following figure, seven variables (r2-r6, A and C) were optimized to locate the transition state. r1 and angle B were kept constant at the product angle since these variables did not vary much from reactant precursor to the optimized geometry of the product, Pt<sub>2</sub>OOH+3H<sub>2</sub>O. The activation energies at 0.8, 1.0 and 1.2 V are 0.15, 0.33 and 0.59 eV respectively. The last value is quite close to the experimental activation energy of 0.44 eV for 4-electron reduction on Pt<sup>10</sup>.



References:

1. R. R. Adzic, in *Electrocatalysis*, J. Lipkowski, and P. N. Ross, Editors, pp.197-242, Wiley, New York (1998).  
2. R. R. Adzic and J. X. Wang, *J. Phys. Chem. B*, **102**, 8988 (1998).  
3. A. B. Anderson and D. B. Kang, *J. Phys. Chem. A*, **102**, 5993 (1998).  
4. A. B. Anderson and T. V. Albu, *Electrochem. Commun.*, **1**, 203 (1999).  
5. A. B. Anderson and T. V. Albu, *J. Am. Chem. Soc.*, **121**, 11855 (1999).  
6. A. B. Anderson and T. V. Albu, *J. Elechthrochem. Soc.*, **147**, (2000).  
7. C. E. Mooney, L. C. Anderson, and J. H. Lunsford, *J. Phys. Chem.*, **97**, 2505 (1993).  
8. B. A. Sexton and A. E. Hughes, *Surf. Sci.*, **140**, 227 (1984).  
9. Y. Y. Yeo, L. Vattuone, and D. A. King, *J. Chem. Phys.*, **106**, 392 (1997).  
10. B. N. Grgur, N. M. Markovic, and P. N. Ross, *Can. J. Chem.*, **75**, 1465 (1997).

Acknowledgement

This research was supported by U. S. Army Research Office, Grant no. DAAD 19-99-1-0253.